Polyesters Resin

Polyesters (Unsaturated)

- The most common type of resin for composites
- The least expensive composite resin
- The easiest-to-cure composite resin
- Polyesters are made from two types of monomers:
  - Di-acids
  - Glycols

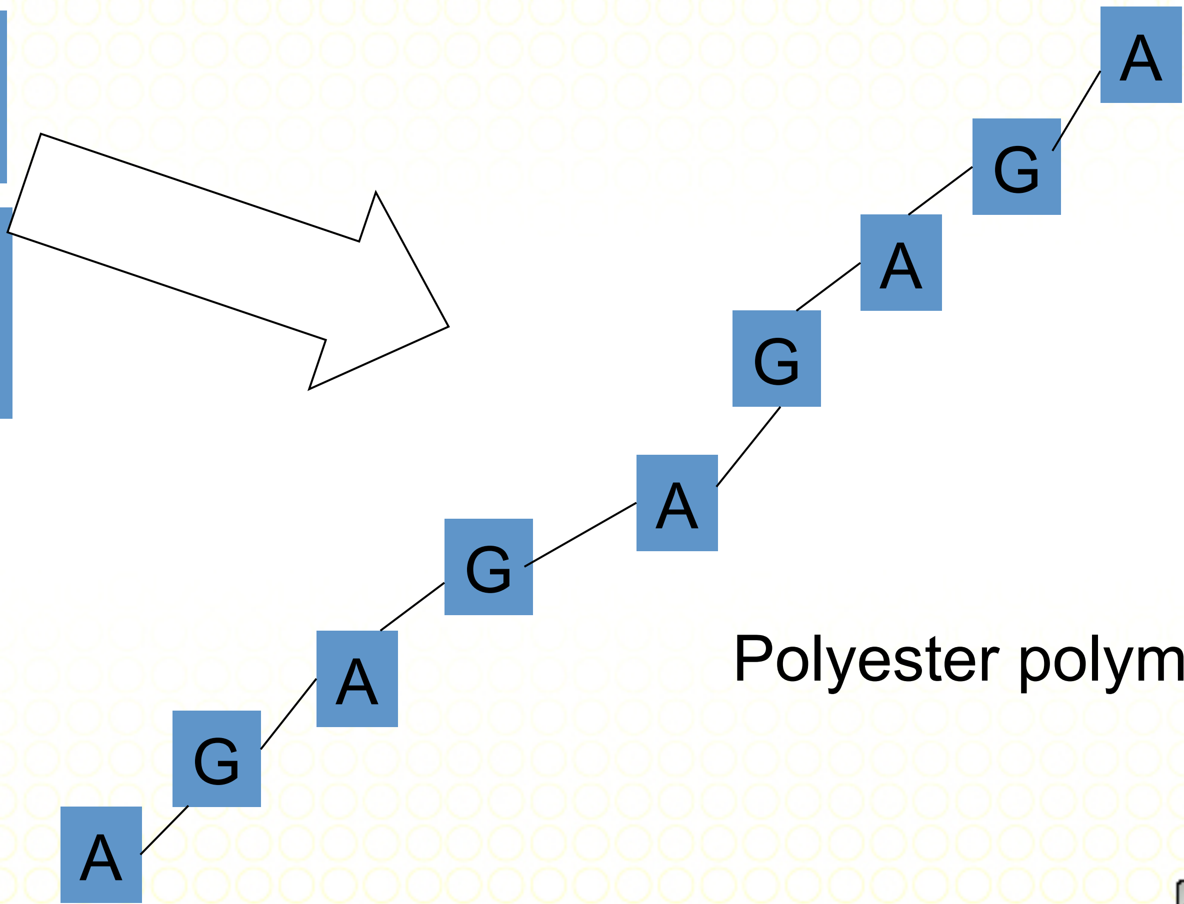
Polyester polymerization

<u>Monomers</u>

Acids A
(di-acids)

Glycols G

(di-alcohols)

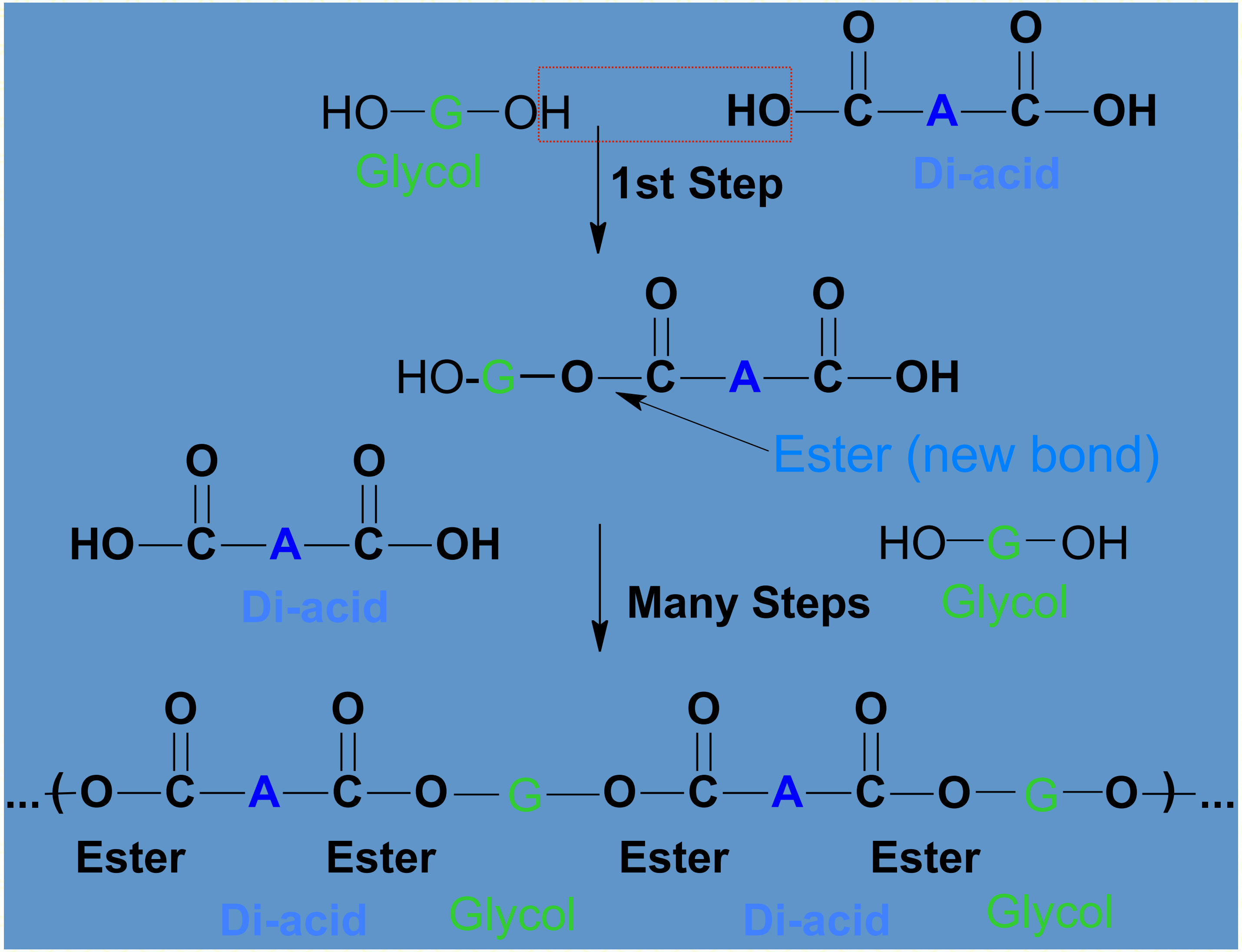


Polyester polymer

Polyester polymerization

- Di-acids have active OH groups on both ends
- Glycols have active H groups on both ends
- One end of the di-acid (the OH group) reacts with one end of the glycol (the H group) to form water (H –OH)
  - The water separates from the polymer and condenses out as a liquid
  - These are condensation polymerization reactions

Polyesters polymerization



Customizing the Polyester – Acids

Di-Acids/Anhydrides	Attributes
Maleic/Fumaric	Unsaturation (crosslink sites)
Orthophthalic	Low cost, styrene compatibility
Isophthalic	Toughness, water/chemical resistance
Adipic	Flexibility, toughness

Customizing the Polyester– Glycols

Glycols	Attributes
Ethylene	Low cost, rigidity
Propylene	Excellent styrene compatibility
Dipropylene	Flexibility, toughness
Diethylene	Flexibility

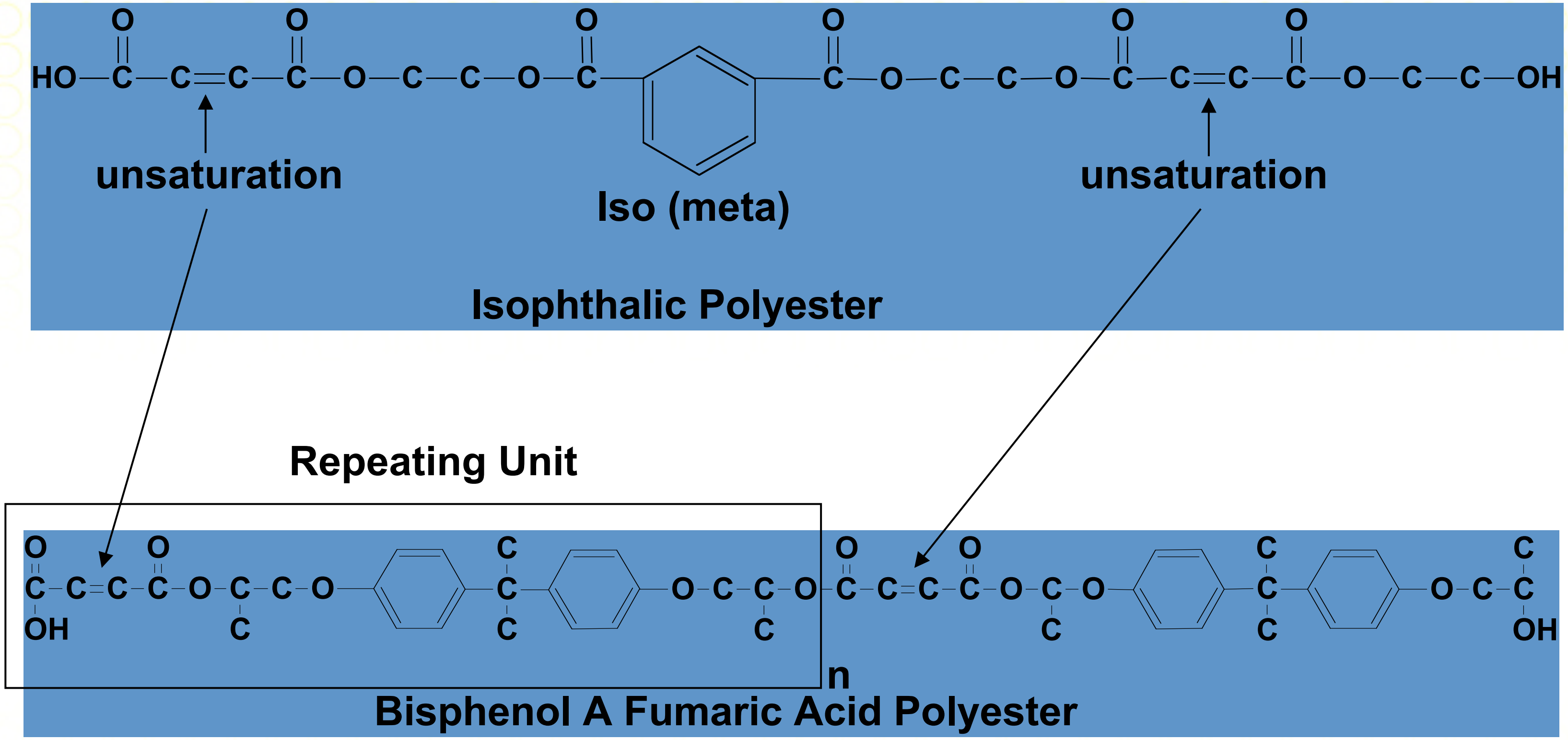
Customizing the Polyester– Solvents

Solvents	Attributes
Styrene	Cost
Vinyl toluene	Strength, stiffness
Acrylic (PMMA)	Low flammability, flexibility

Customizing the Polyester– Adding Other Monomers or Resins

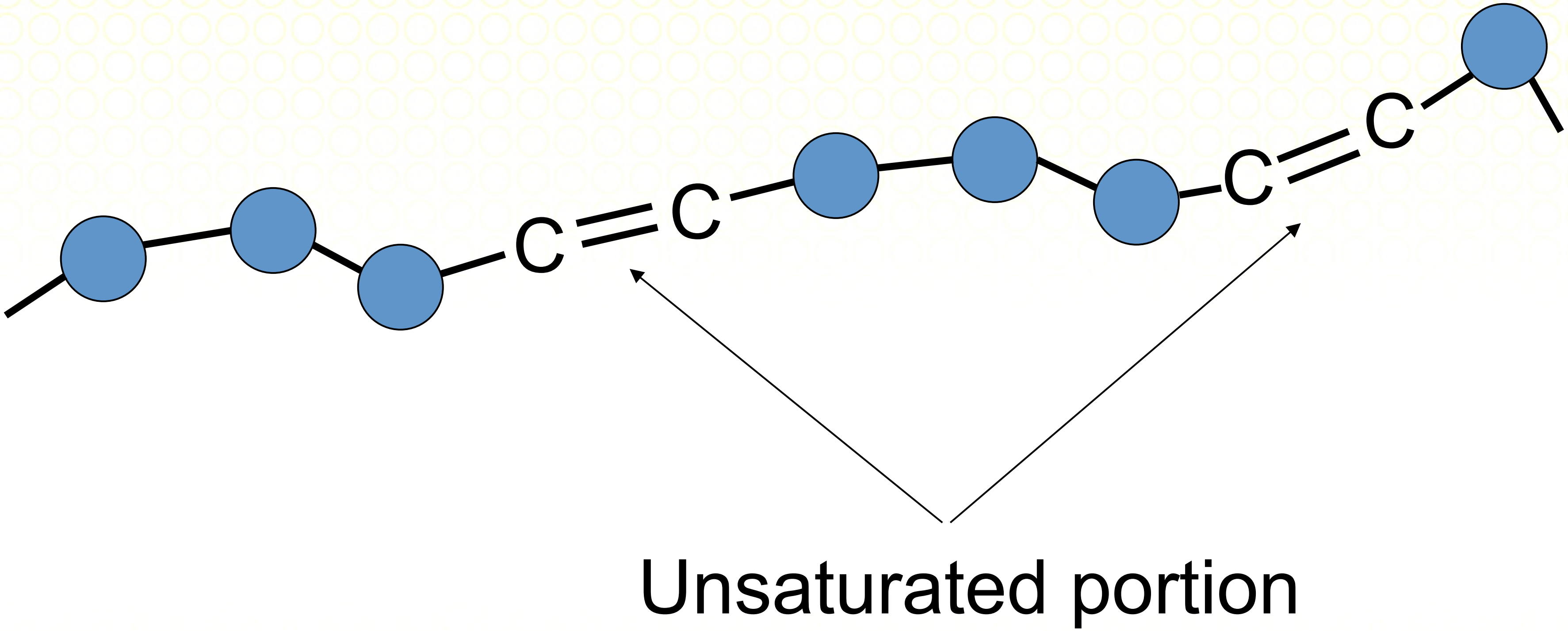
Resin	Purpose
Dicyclopentadiene (DCPD)	Lower cost, improve stiffness
Styrene butadiene rubber (SBR)	Toughness
Thermoplastics	Surface quality

Polyesters – specific molecules



The number of repeating units is usually shown by an n

Polyesters – crosslinking (curing)

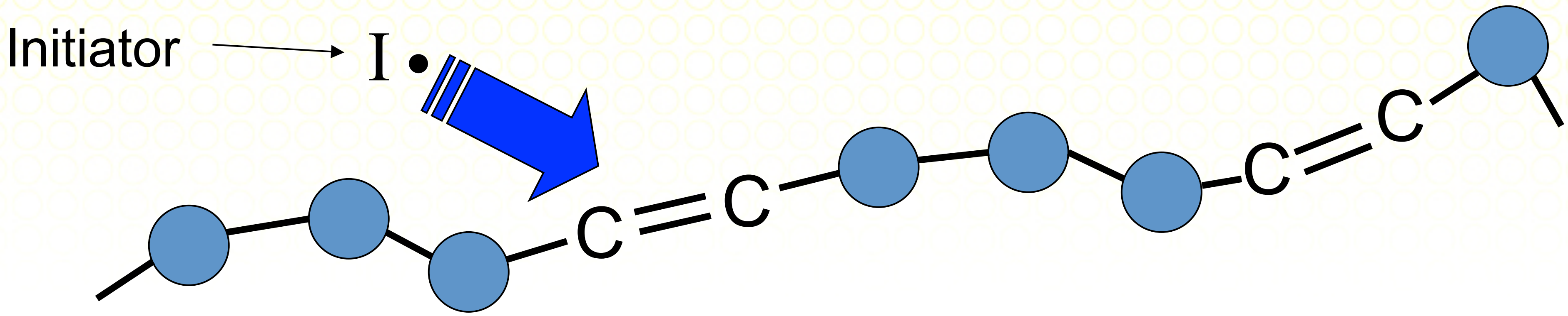


Polyesters must have unsaturated portions to crosslink

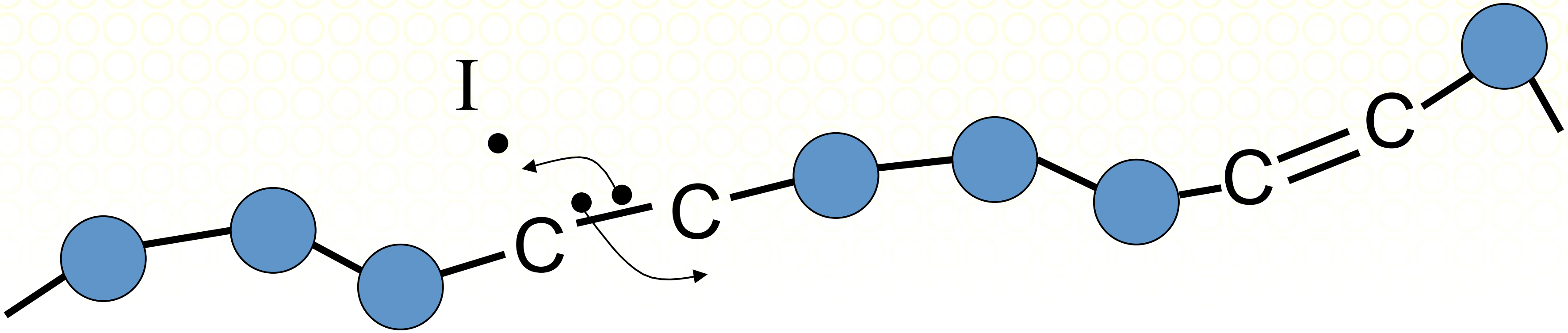
Initiators (catalysts)

- Initiators are sometimes called **catalysts**.
- The crosslinking reaction is begun when an **initiator** reacts with the double bond.
- The most common initiators are **peroxides**.
- The peroxides are effective initiators because they split into **free radicals** (that is, they have unshared electrons) which react easily with the double bonds.
- Free radicals have **unshared electrons**.

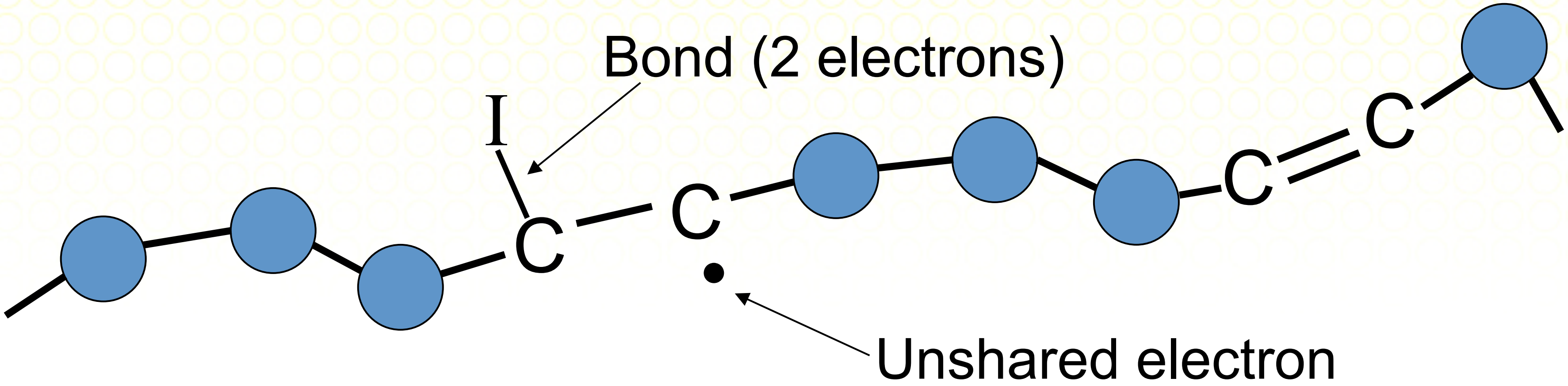
Polyesters – crosslinking (curing)



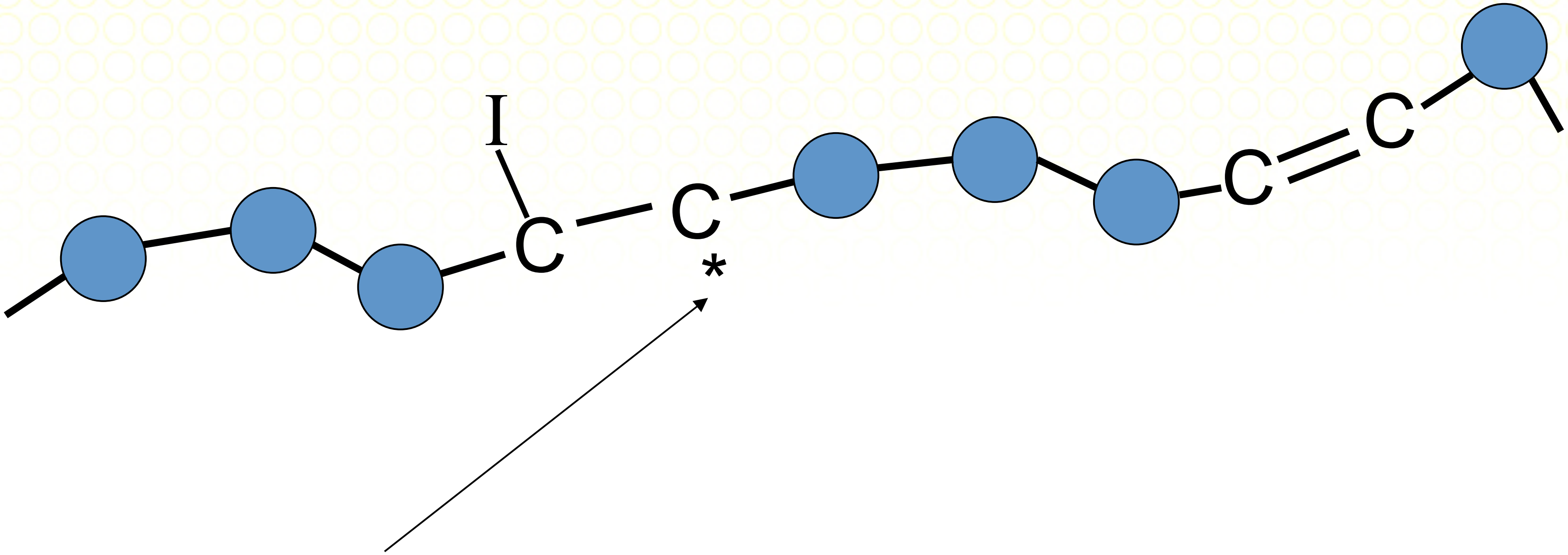
Polyesters – crosslinking (curing)



Polyesters – crosslinking (curing)



Polyesters – crosslinking (curing)



Free radical (unshared (unbonded) electron)

Free radicals react readily with any Carbon-carbon double bond they encounter

Polyesters – Reaction Problem

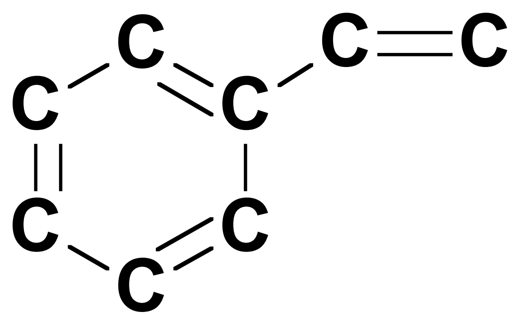
- To react and form a crosslink, the free radical on the polymer needs to encounter (**collide with**) a double bond on another polymer
- The polymers are long and entangled (highly **viscous**), thus they don't move very quickly
- The polymers are **bulky** and it is hard to get the free radical into the area of the double bond

Polyesters – Reaction Solution

- Dissolve (**dilute**) the polymer with a solvent so that the polymers can move around freely
  - Ideally, the solvent will **react** during the crosslinking reaction so that it does not need to be removed from the solid
    - These types of solvents are called "**reactive solvents**" or "**reactive diluents**" or "**co-reactants**"
- Added benefit:
  - The solvent will also reduce the viscosity so that the polymer will **wet the fibers** more easily

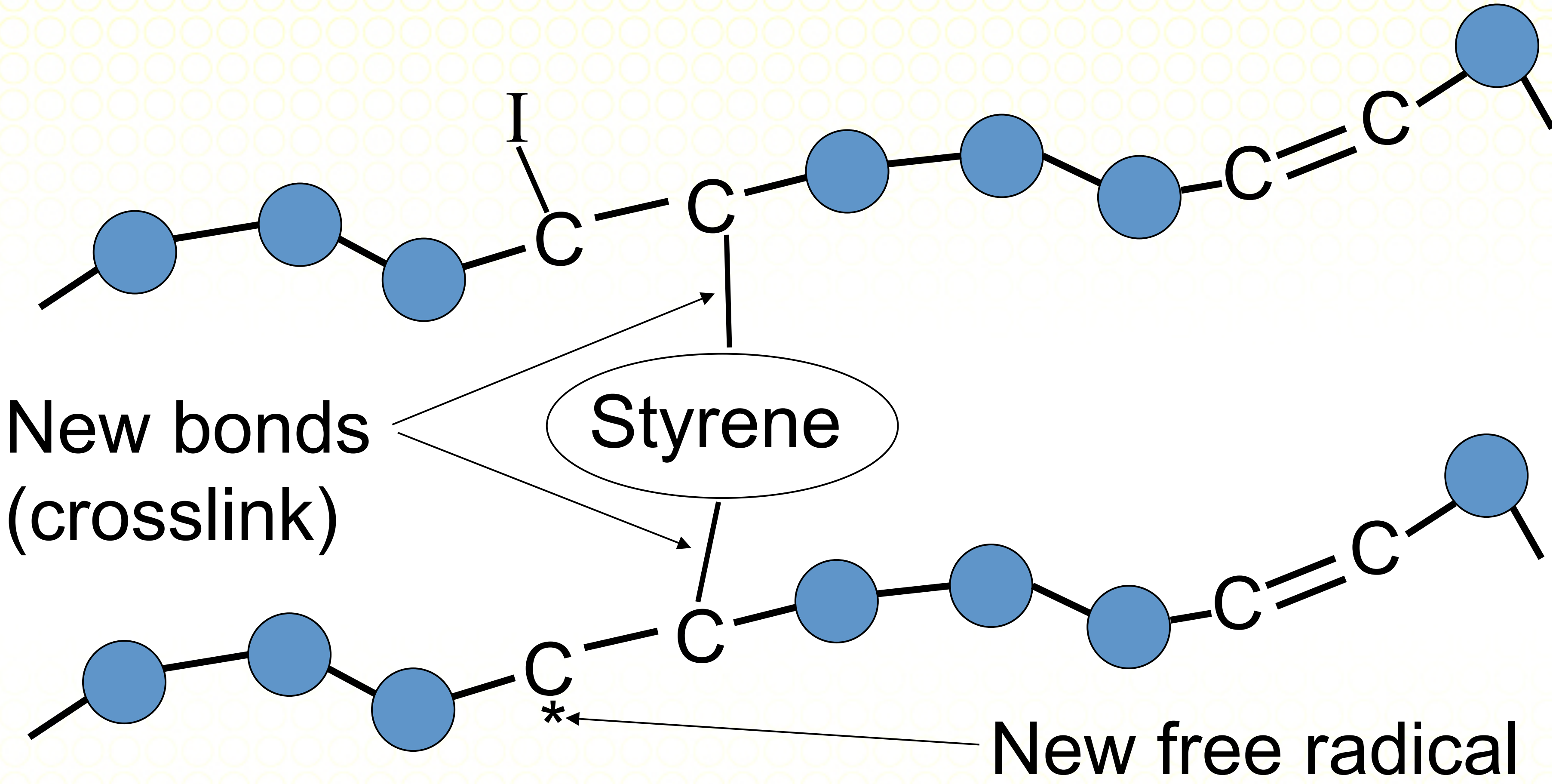
Styrene

- Styrene is the most common solvent for polyesters
- The styrene **reacts** (is consumed) during the crosslinking reaction because the styrene contains a double bond and reacts with the free radical



- The styrene serves as a **bridge molecule** between the polymer chains (as part of the crosslink)
  - There may be as many as 8 styrene molecules in a bridge

Polyester – forming the crosslink



The styrene is a bridge molecule between the polyester polymers

The new free radical is available to react with another styrene

Crosslinking Reaction

- Called **addition** or **free radical** crosslinking reaction
- Proceeds as a **chain reaction**
  - Once started, it will keep going unless specifically terminated
  - Doesn't need more initiator
  - Makes its own reactive sites

Inhibitors

- Inhibitors are added, usually by the resin manufacturer, to **slow down** the crosslinking reaction
  - Inhibitors typically **absorb free radicals**
  - Inhibitors **protect the polymer** during storage because sunlight, heat, contaminants, etc. can start the curing reaction
  - Molders must **add sufficient initiator** to overcome the inhibitors and to cause the crosslinking to occur

Promotors (accelerators)

- Added to the polymer to make the initiator work more efficiently or at a **lower temperature**
  - Each type of peroxide has a temperature at which it will break apart into free radicals
  - These temperatures are usually above room temperature
  - For room temperature curing, a chemical method for breaking apart peroxides is needed
- The most common promoters (accelerators) are **cobalt compounds and analines (DMA)**
- **Never** add a promoter directly into an initiator

Additives

- Additives are components (usually minor) that have various functions that are not related to the curing reaction
- The most common types of additives are:
  - Fillers (to lower cost and/or give stiffness)
  - Pigments
  - Fire retardants
  - Surfactants (to promote surface wetting)
  - UV inhibitors/Anti-oxidants

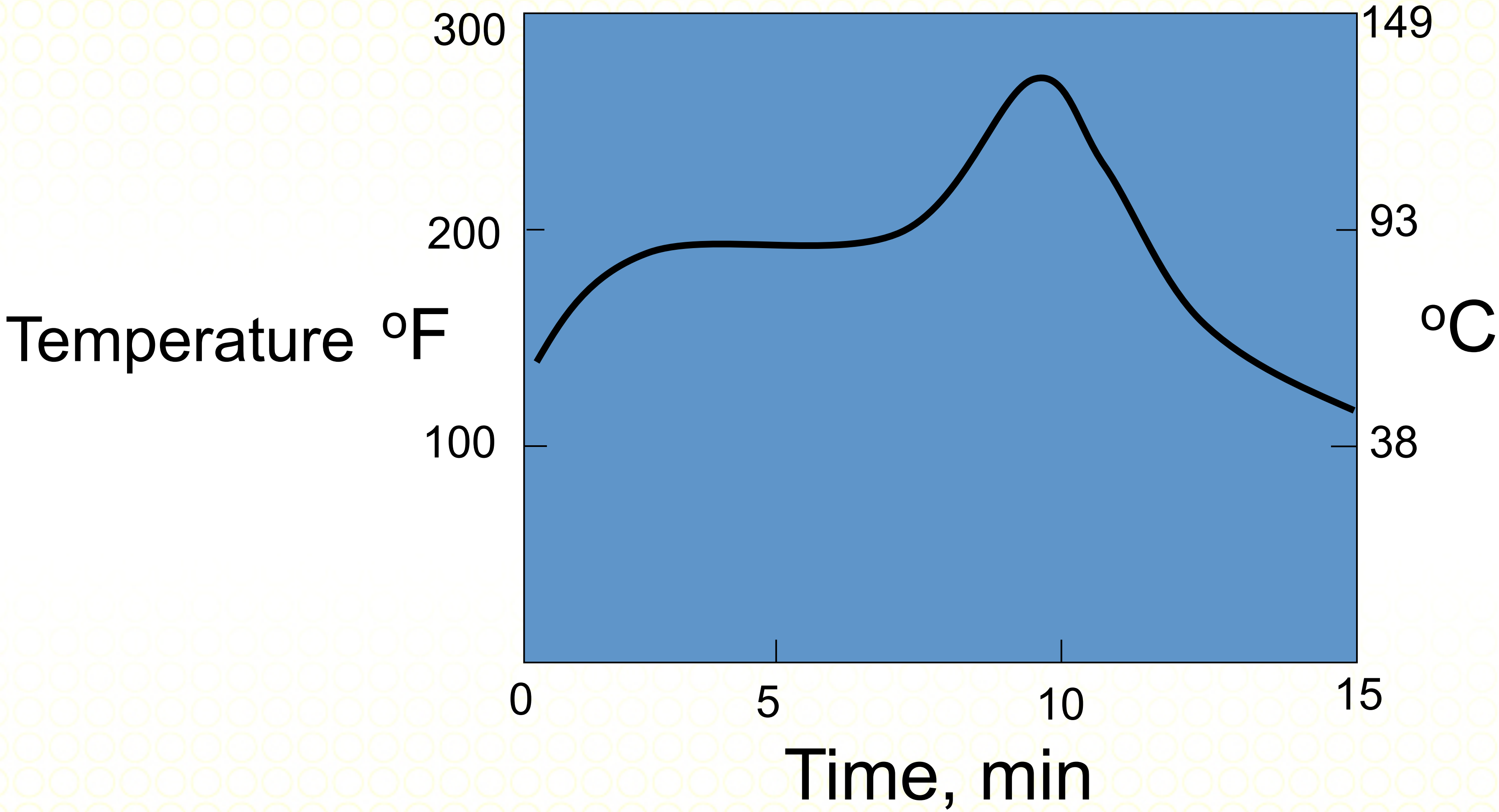
Factors influencing cure

- Mix ratios
  - Resin, initiator, inhibitor, accelerator, solvent
  - Fillers, pigments, other additives
- Storage time after activation
- Thickness of the part
- Cure time
- Humidity
- Temperature

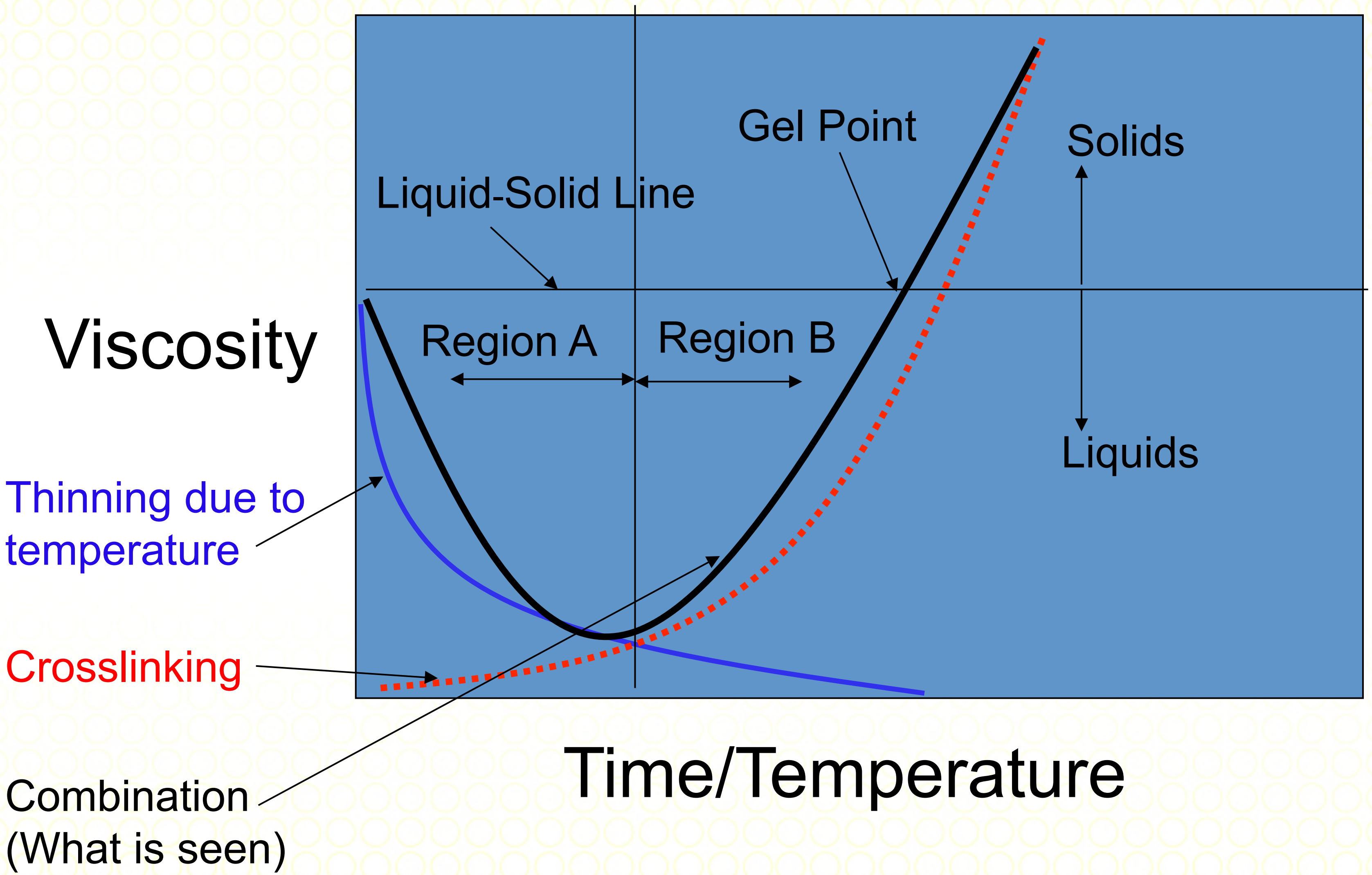
Thermal effects

- The **rate** (speed) of chemical reactions increases as the temperature is increased
- Molecular **collisions** are required
- Heat increases molecular movement
- Highly reactive entities (like free radicals) have successful reactions with almost every collision

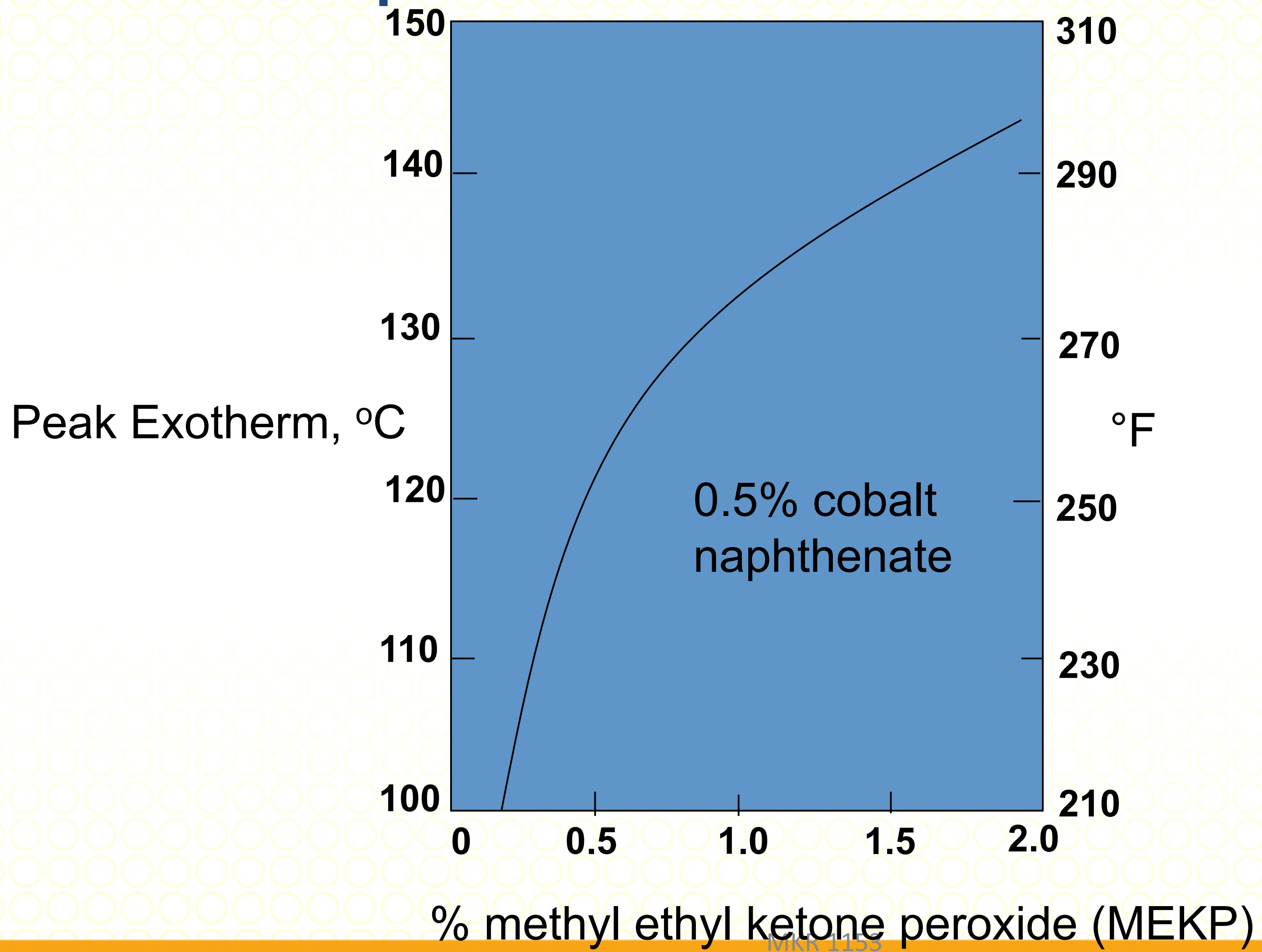
Time-Temperature Curve in the sample at constant applied temperature



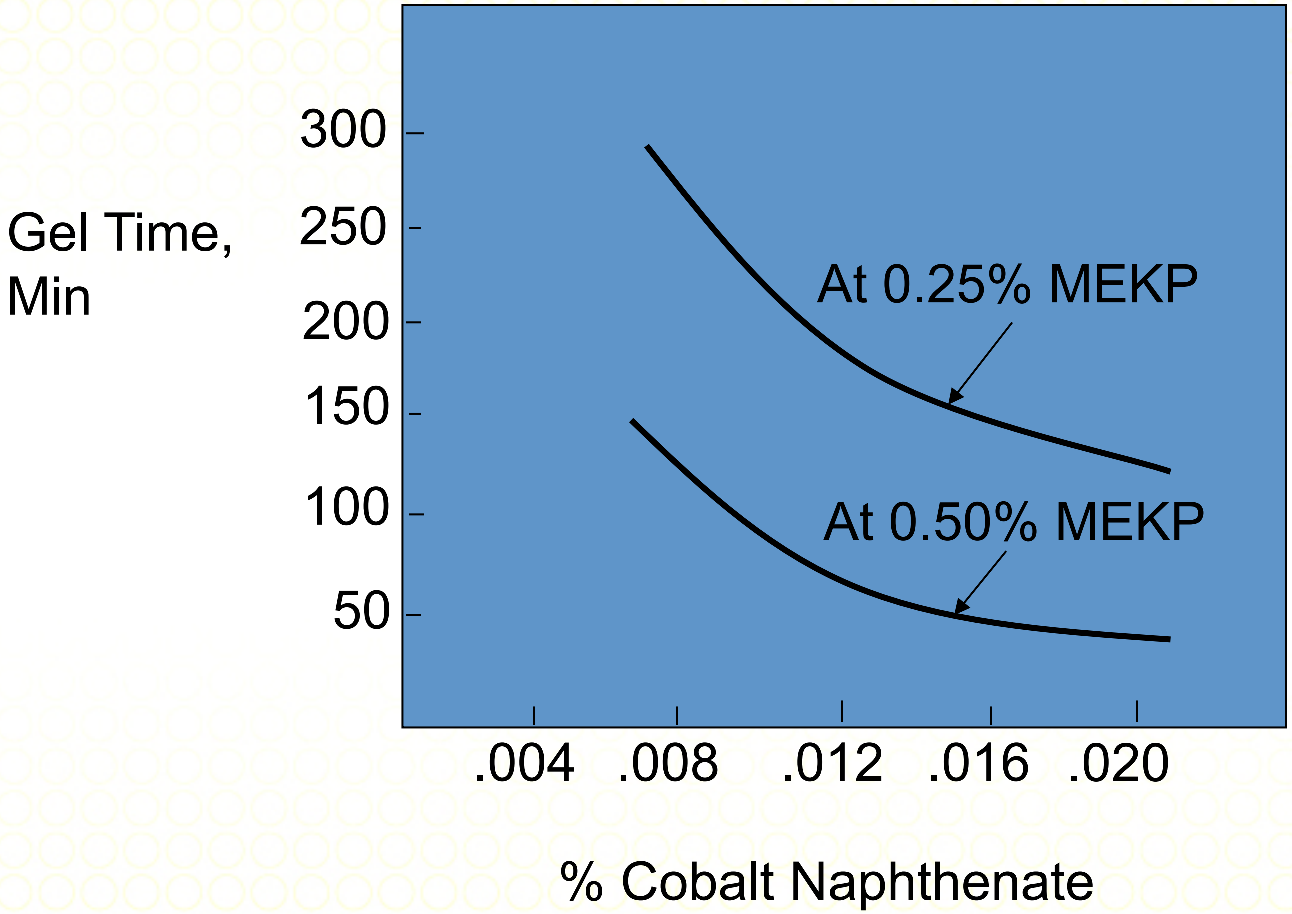
Temperature-Viscosity Curve



Peroxide content – Temperature and Time Curves



Accelerator Content – Time Curve



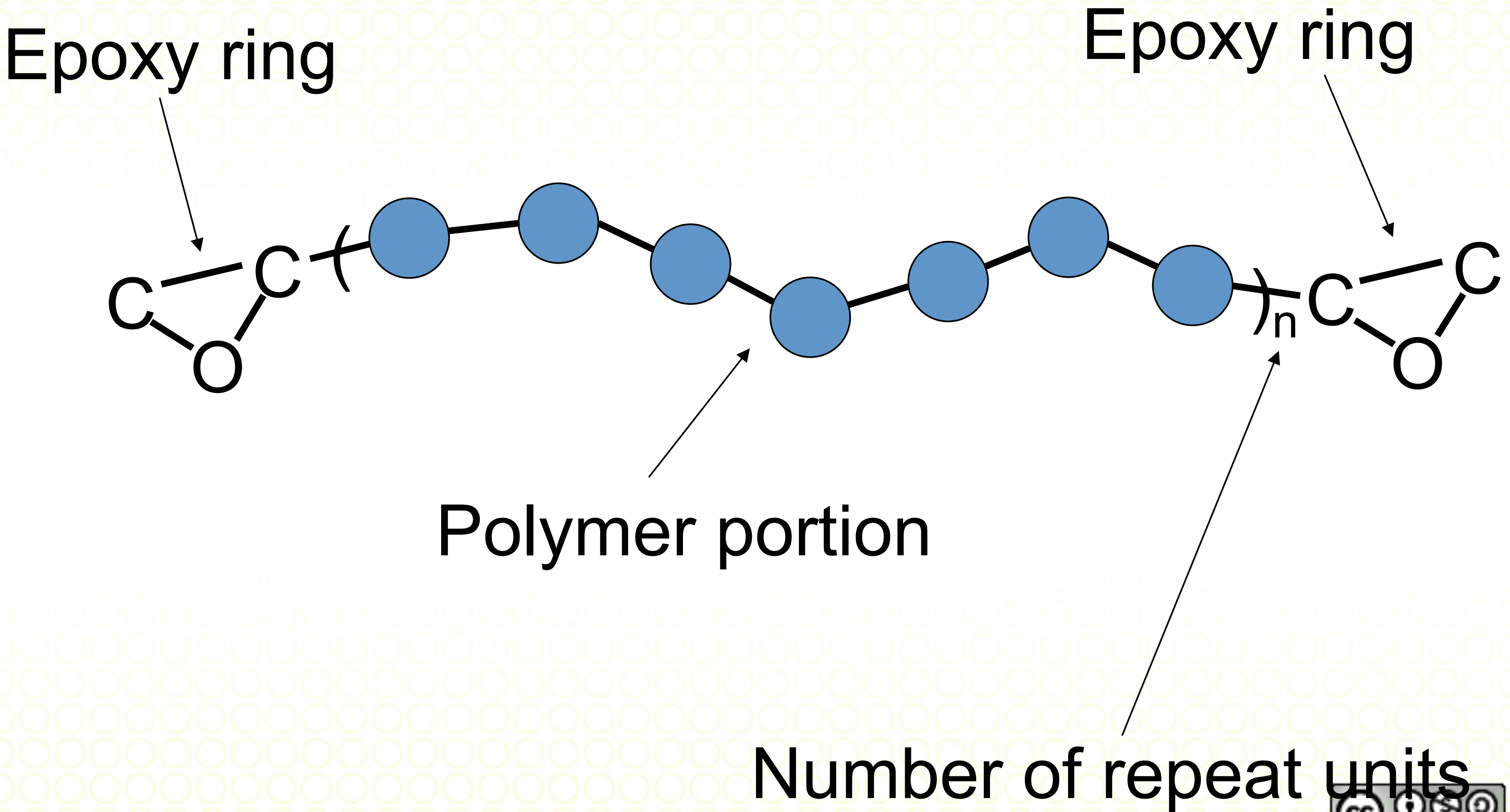
Polyesters

Epoxies

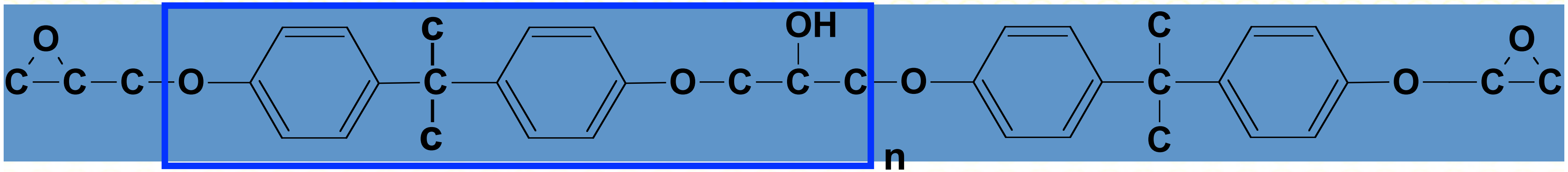
Epoxies

- **Second** most widely used family of thermosets (after polyesters)
- Large portion of uses are **non-reinforced** (adhesives, paints, etc.)
- **Circuit boards** are the largest reinforced application (low conductivity, low volatiles)
- **Advanced composites** use epoxies because of
  - Thermal stability
  - Adhesion
  - Mechanical properties

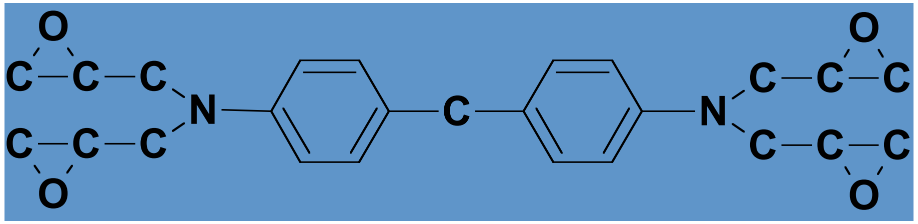
Epoxy Structure



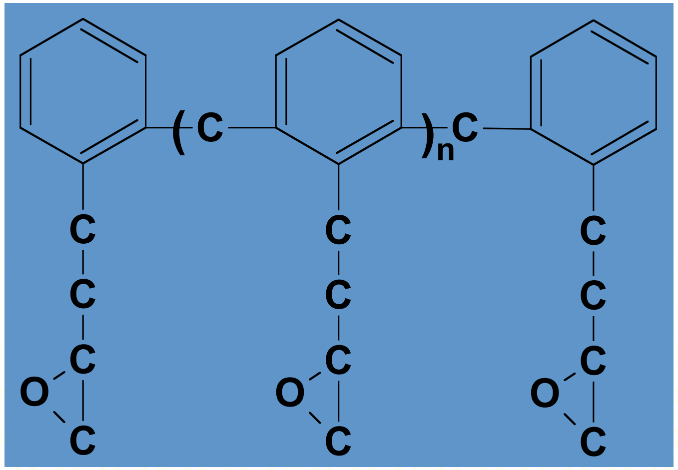
Epoxy – specific molecules



a) Diglycidyl Ether of Bisphenol A (DGEBPA)

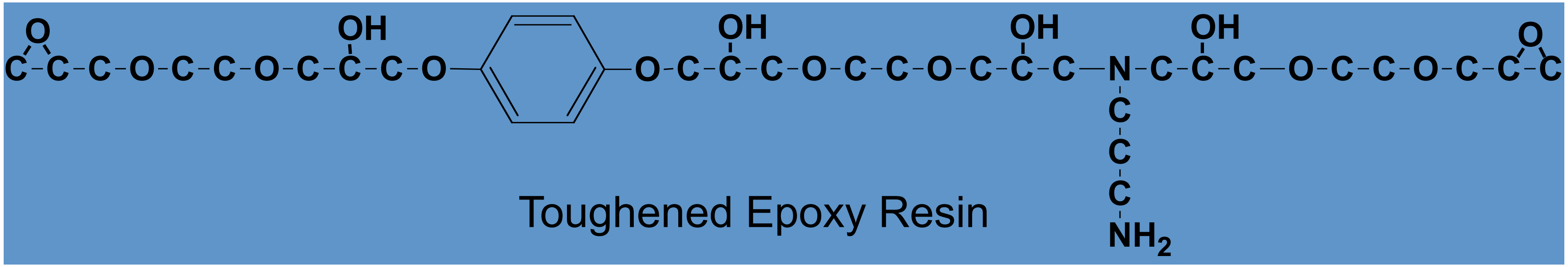


b) Tetraglycidylmethylenedianiline (TGMDA)

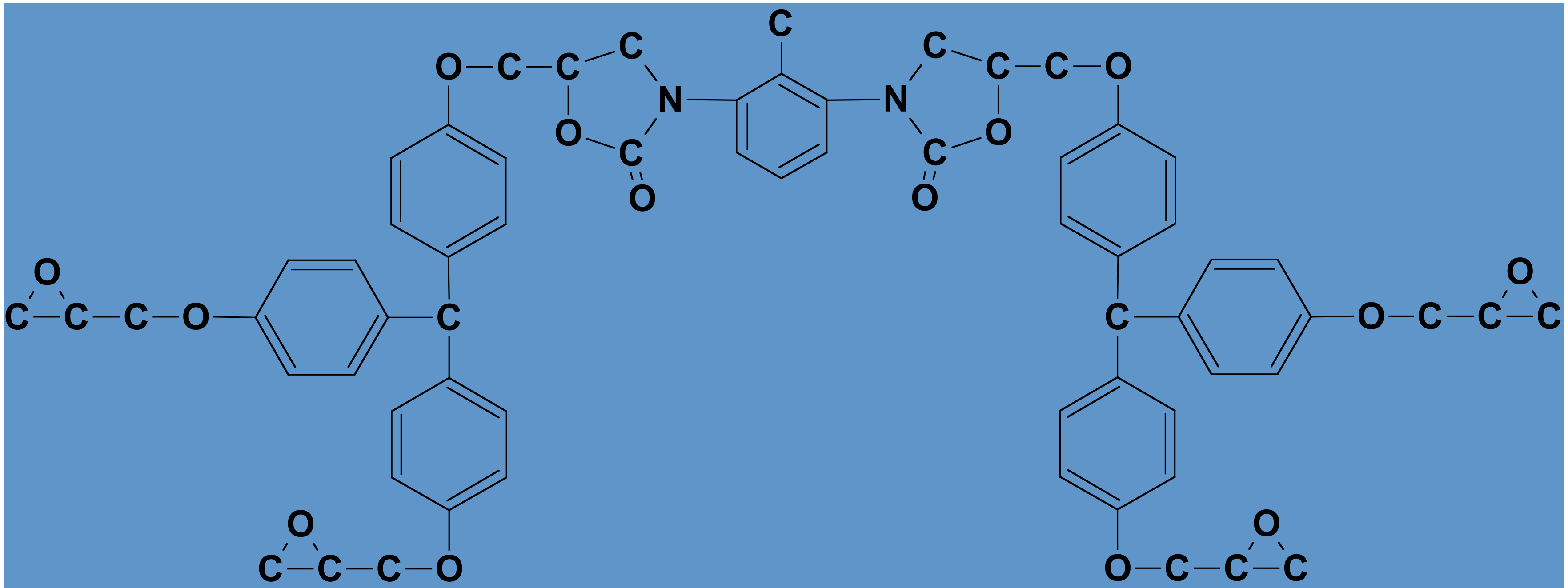


c) Epoxidized phenolic resin (Epoxy Novalac)

Epoxy – specialty molecules



Toughened Epoxy Resin

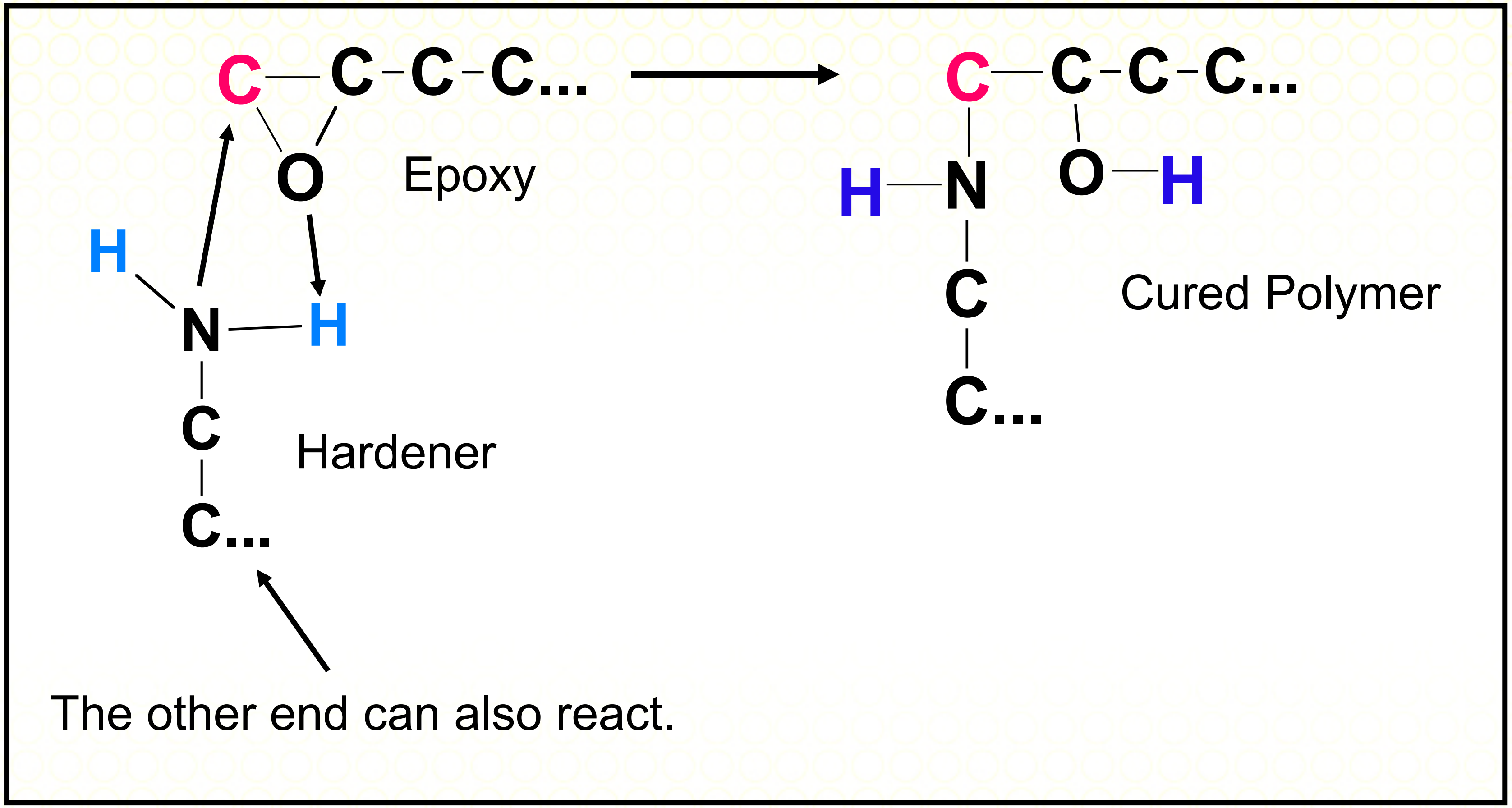


High Temperature Epoxy Resins

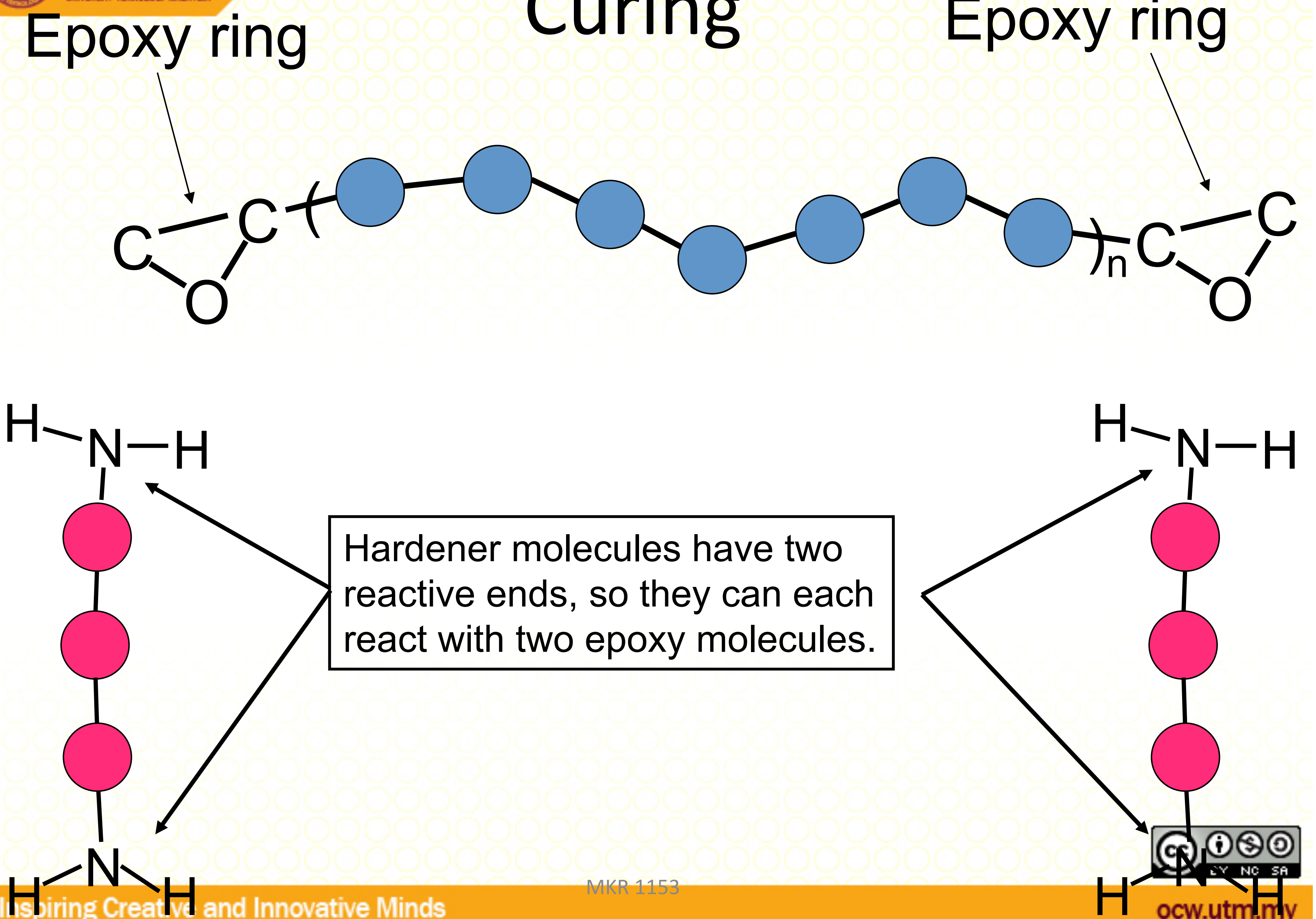
Curing Epoxies

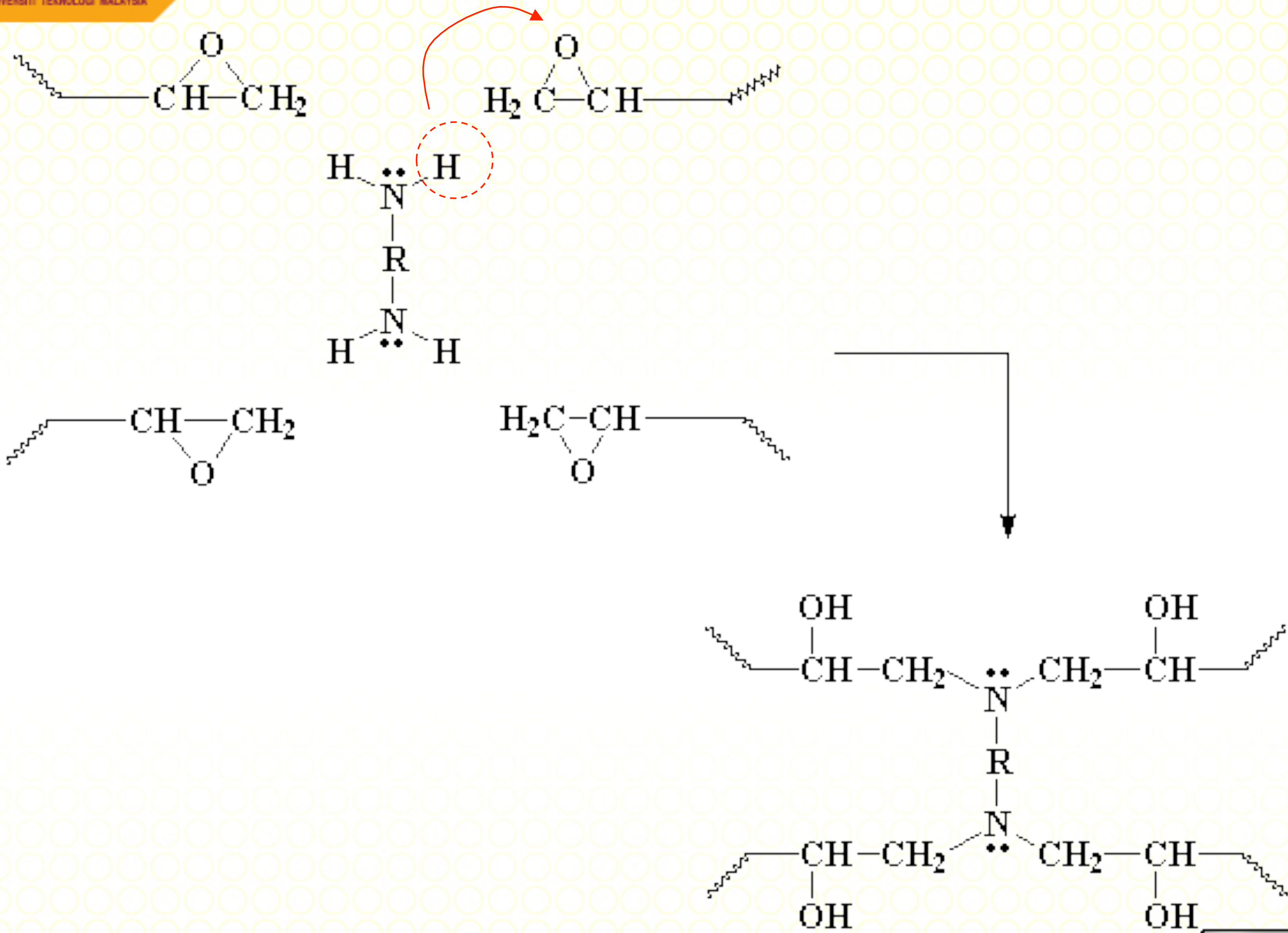
- Epoxies use hardeners instead of initiators for curing
- Hardeners can be almost any molecule that will react with (open) the epoxy ring

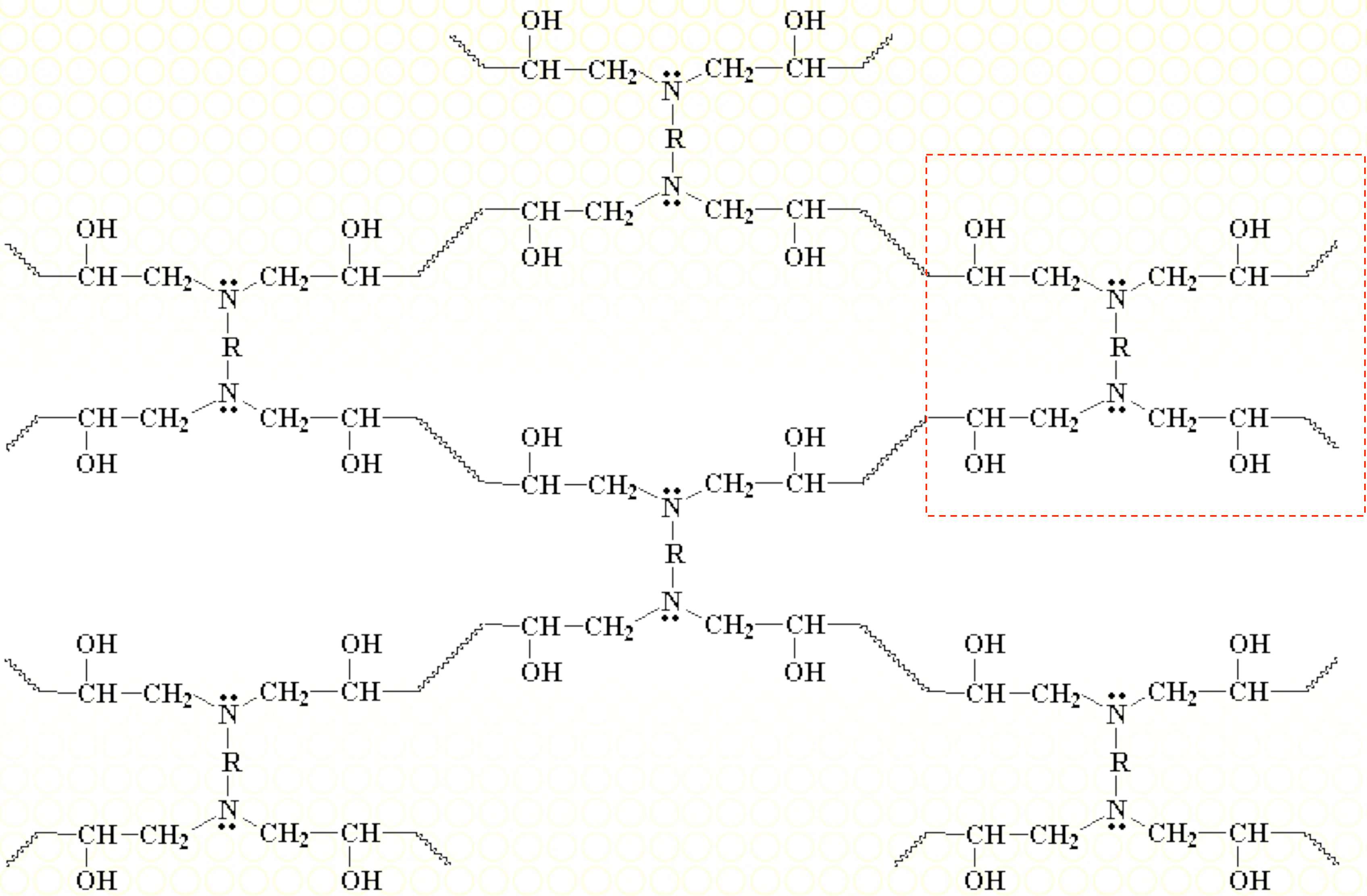
Epoxy Crosslink Mechanism



Curing


Epoxy ring
Epoxy ring
C
C
O
n
C
C
O
H
N
H
H
N
H
H
N
H
H
N
H
Hardener molecules have two reactive ends, so they can each react with two epoxy molecules.

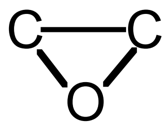

O
CH–CH₂
O
H₂C–CH
H
N
H
R
N
H
H
CH–CH₂
O
H₂C–CH
O
OH
OH
CH–CH₂
N
CH₂–CH
R
N
CH–CH₂
CH₂–CH
OH
OH


OH
CH
CH2
N
R
CH2
OH

Effects of various hardeners

Hardeners	Advantages	Disadvantages
Aliphatic amines	Convenience, low cost, room temp cure, low viscosity	Skin irritant, critical mix ratios, blushes
Aromatic amines	Moderate heat resistance, chemical resistance	Solids at room temp, long and elevated cures
Polyamides	Room temp cure, flexibility, toughness, low toxicity	High cost, high viscosity, low HDT
Amidoamines	Toughness	Poor HDT
Dicyandiamide	Good HDT, good electrical	Long, elevated cures
Anhydrides	Heat and chem resistance	Long, elevated cures
Polysulfide	Moisture insensitive, quick set	Odor, poor HDT
Catalytic	Long pot life, high HDT	Long, elevated cures, poor moisture
Melamine/form.	Hardness, flexibility	Elevated temp cure
Urea/form.	Adhesion, stability, color	Elevated temp cure
Phenol/form.	HDT, chem resistance, hardness	Solid, weatherability

Epoxy and Polyester Comparison

Comparisons	Polyester	Epoxy
Active site	C=C	
Crosslinking reaction	Addition/free radical	Ring opening
Crosslinking agent	Initiator (peroxide)	Hardener
Amount of x-link agent	1-2% of resin	1:1 with resin
Solvent/viscosity	Styrene (active)/low	Infrequent/high
Volatiles	High	Low
Inhibitors, accelerators	Frequent	Infrequent
Reactant toxicity	Low	Moderate
Cure conditions	Room temp or heated	Heated (some room)
Shrinkage	High	Low
Post cure	Rare	Common

Polyester and Epoxy – Properties

Property	Polyester	Epoxy
Adhesion	Good	Excellent
Shear strength	Good	Excellent
Fatigue resistance	Moderate	Excellent
Strength/stiffness	Good	Excellent
Creep resistance	Moderate	Moderate to good
Toughness	Poor	Poor to good
Thermal stability	Moderate	Good
Electrical resistance	Moderate	Excellent
Water absorption resist	Poor to moderate	Moderate
Solvent resistance	Poor to moderate	Good
UV resistance	Poor to moderate	Poor to moderate
Flammability resistance	Poor to moderate	Poor to moderate
Smoke	Moderately dense	Moderately dense
Cost	Low	Moderate

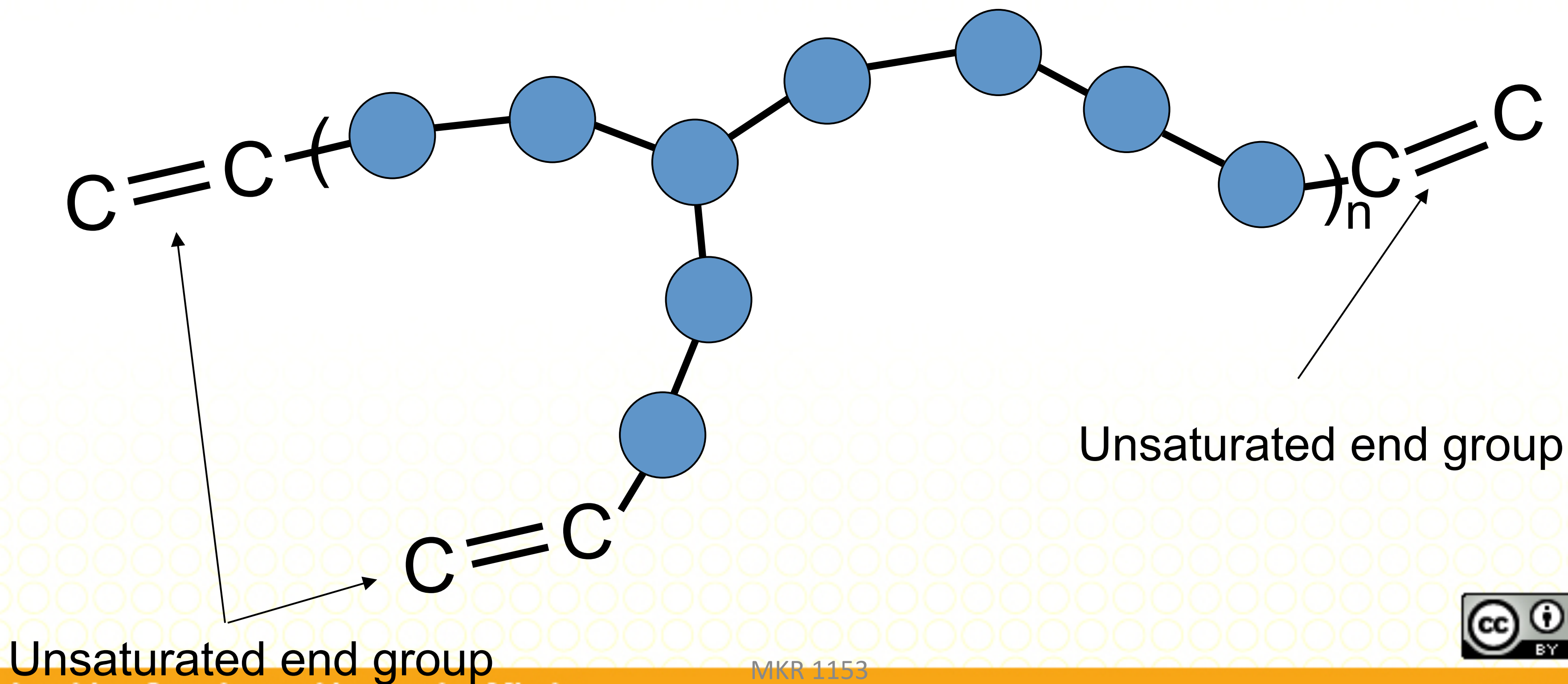
Epoxy

Vinyl Ester Resins

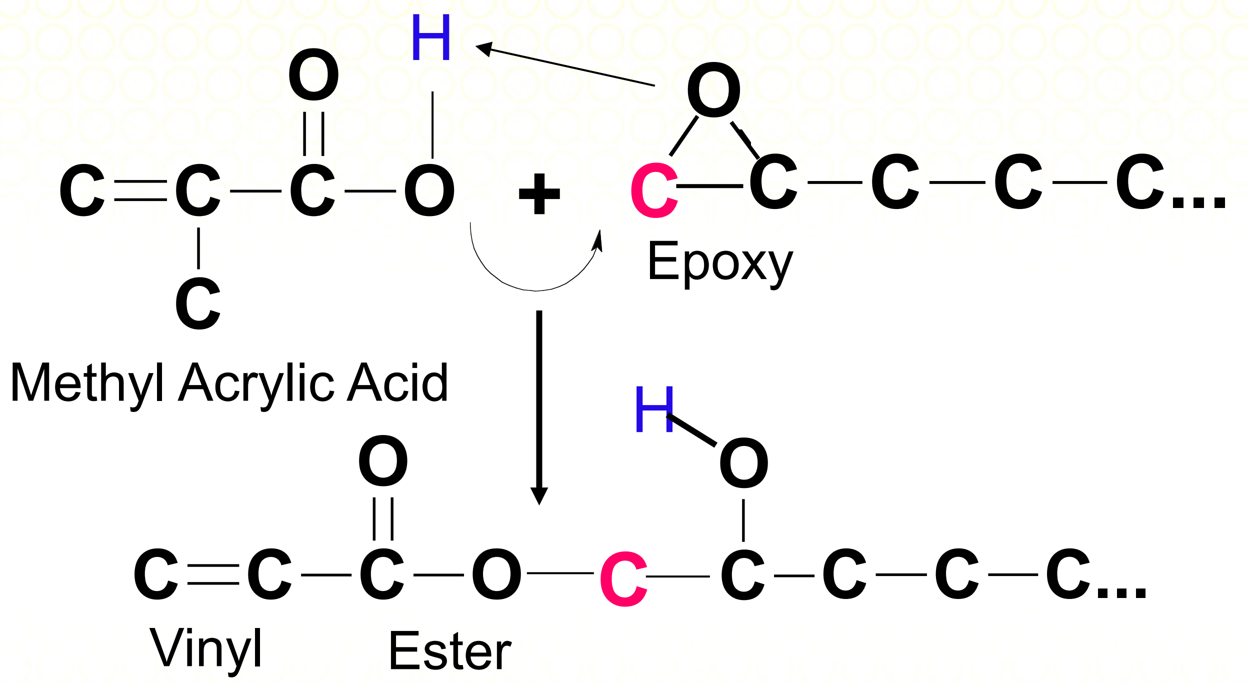
Vinyl Esters

- Epoxy resins that have been **modified** so that they can be **cured like a polyester**
  - The modification is usually a reaction with an acrylic (**acrylic modified epoxy**)
  - The modification must substitute a carbon-carbon **double bond** for the epoxy ring

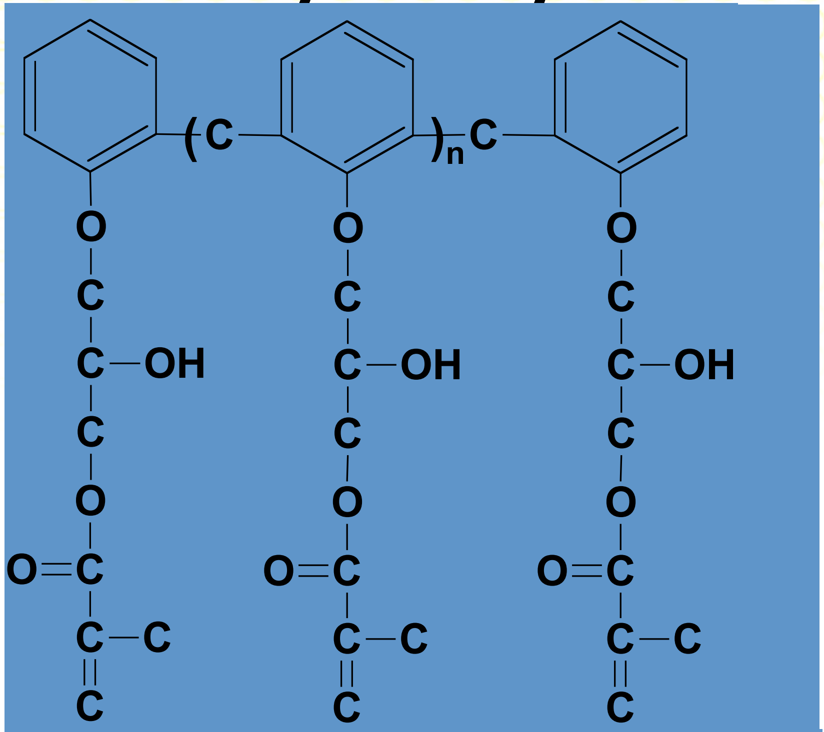
Vinyl Ester Structure



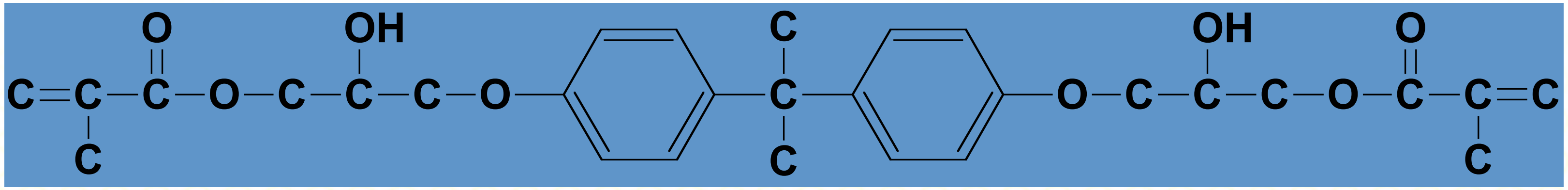
Vinyl esters – specific molecules



Specialty Vinyl Esters



Epoxy Novolac Vinyl Ester Resin



Bisphenol-A Epichlorohydrin-based vinyl ester

Vinyl esters – Properties

- Almost all properties of vinyl esters (and cost) are **intermediate** between polyesters and epoxies
- Some of the most important properties include:
  - Water and chemical resistance
  - Electrical stability
  - Thermal stability
  - Toughness
  - Low volatiles during manufacture
  - Low shrinkage

Vinyl Esters

[Epoxy adhesive]()